GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

October 31, 1962

Commanding Officer
U. S. Army Research Office (Durham)
Box CM, Duke Station
Durham, North Carolina

Subject: Progress Report No. 1, Project No. A-606
"Photochemically Induced Reactions of Acetylenes with Aromatic Compounds", Covering the Period from January 2 to September 30, 1962
Grant No. DA-APO(D)-31-124-G258

Gentlemen:

The previously reported reaction product[1] from irradiation of naphthalene and dimethyl acetylenedicarboxylate in acetone with ultraviolet light has been partially separated by preparative vapor phase chromatography. The two chief products have retention times of 3.7 and 13.4 minutes. Attempts to crystallize either of these two fractions have so far been unsuccessful. The fraction, of retention time 13.4 minutes, upon reaction with benzylamine gave a crystalline N-benzylamide, m.p. 259.3-260.0°, which has satisfactory C, N, and N-analyses for $C_{28}N_{24}N_2O_2$ as expected for an N, N'-dibenzyl amide of a one to one adduct of naphthalene and dimethyl acetylenedicarboxylate. Dilute solutions of this amide in acetonitrile when treated with Br_2 or $KMnO_4$ and gave no decoloration. The amide shows strong absorption of ultraviolet light near 288 mμ ($\epsilon = 1.0 \times 10^4$) and weaker absorption maxima at 316.5 and 320 mμ ($\epsilon = 830$ for the last maximum). The

[1] Final Report Project No. A-547, Grant No. DA-ORD-31-124-61-G67, Department of the Army Project No. 59901004, Ordnance Corps R & D. Project No. TB2-0001, U. S. Army Research Office (Durham) Project No. 2123-C.

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infrared spectrum confirmed that the compound was a secondary amide (amide I and II bands at 6.1 and 6.5 μ respectively). The nuclear magnetic resonance spectrum of the amide in the solvent trifluoro-acetic acid contained a doublet at the position expected for the benzyl hydrogens of the N-benzyl groups. This result may mean that the benzyl groups are in non-equivalent positions since the N, N'-dibenzyl amide of naphthalene -2,3-dicarboxylic acid gives but a single peak for the benzylic hydrogen atoms in trifluoro-acetic acid solution. The NMR spectrum of the unknown amide shows complex absorption in the aromatic region; it is hoped that a more highly resolved spectrum can be obtained in CF_3CO_2D as solvent. This and other work on the structure of the adducts from naphthalene and dimethyl acetylenedicarboxylate are continuing.

We have confirmed the report[2] that irradiation of a solution of acetylene in benzene-acetone gives a complex mixture of products containing only a trace of cyclooctatetraene. We find that the concentration of cyclooctatetraene produced does not exceed 0.02% by volume and that the concentration of cyclooctatetraene is not increased by increasing the time of irradiation from 4 to 16 hours. Moreover irradiation of a 0.6% solution of cyclooctatetraene in benzene-acetone solution for 18 hours resulted in essentially complete destruction of the cyclooctatetraene.

A graduate research assistant has been employed in only three out of the past nine months. This reduced rate of effort is due in part to the difficulty of obtaining a suitable research assistant but is largely due to

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[2] D. Bryce-Smith and J. E. Lodge, Proc. Chem. Soc., 333 (1961).

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the difficulty of working in our present laboratory area because of the construction of a third floor on our building. We plan to move into these new laboratories on or before January 1, 1963, and it is hoped that our work can proceed at full rate during the coming year.

Respectfully submitted,

Erling Grovenstein, Jr.
Project Director

Approved:

Frederick Bellinger, Chief
Chemical Sciences & Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

May 24, 1963

Commanding Officer
U. S. Army Research Office (Durham)
Box CM, Duke Station
Durham, North Carolina

Subject: Progress Report No. 2, Project No. A-606
"Photochemically Induced Reactions of Acetylenes with Aromatic Compounds," Covering the Period from October 1, 1962 to March 31, 1963
Grant No. DA-AP0(D)-31-124-G258

Gentlemen:

Because of the unavailability of a graduate student as a research assistant during the period of the present report, there is little progress to report. The Chief Investigator has now moved to, and become established in, new laboratories on the third floor of Daniel Laboratory of Chemistry. A new quartz cell has been purchased which should greatly facilitate our irradiations with ultraviolet light. All is therefore in readiness to proceed with our program of research. The Chief Investigator will devote full-time effort for two months during the coming summer toward prosecution of this program of research, and a graduate student has been employed as a research assistant to start work in September of this year.

Respectfully submitted,

Erling Grovenstein, Jr.
Chief Investigator

Approved:

Frederick Bellinger, Chief
Chemical Sciences & Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA 13, GEORGIA

September 27, 1963

Commanding Officer
U. S. Army Research Office (Durham)
Box CM, Duke Station
Durham, North Carolina

Subject: Progress Report No. 3, Project No. A-606
"Photochemically Induced Reactions of Acetylenes with Aromatic Compounds", Covering the Period from April 1, 1963 to September 20, 1963
Grant No. DA-AP0(D)-31-124-G258

Gentlemen:

Work has continued on the photochemical reaction of naphthalene with dimethyl acetylenedicarboxylate. The reaction has been run in both acetone and methyl alcohol as solvent with qualitatively similar results. In previous work the products have been separated by distillation at about 50 microns pressure (150 to 260°) and by vapor phase chromatography (vpc)(at 225°). Since observations suggest that some thermal decomposition takes place under these conditions, the reaction products have now been separated by liquid phase chromatography on silicic acid, into two major fractions. Fraction A, which is of short retention time, amounts to some 15% and Fraction B, which is of long retention time, amounts to some 50% of the material which was eluted from the column. Fraction A was analyzed by vpc with the results shown in Table I. Fraction A, as far as is known, appears to be stable under the conditions of the vpc analysis; however, Fraction B, which is obviously of higher molecular weight, appears to decompose under the conditions of such vpc analysis since this fraction gives much material of shorter retention time than observed for Fraction A.

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TABLE I

Vapor Phase Chromatography of Fraction A
on Perkin-Elmer Column O at 246°

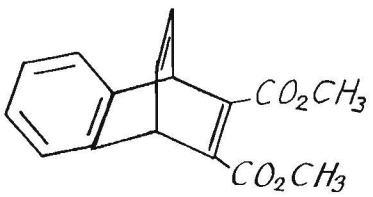
Rentention Time (min.)	Percentage*
5.6	18
6.7	8.7
7.5	6.0
8.7	50
10.3	4.0
12.5	13

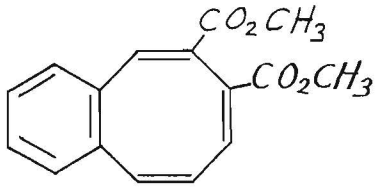
* Based on peak areas and the assumption of equal thermal conductivities for all components.

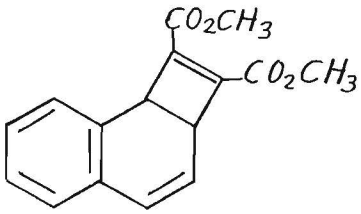
Fraction A, upon reaction with benzylamine, gave some 17% yield of the N_1N-dibenzyl amide, $C_{28}H_{24}N_2O_2$ previously reported.[1] This colorless amide is evidently derived from the major component (retention time 8.7 min.) of Fraction A. Saponification of Fraction A by KOH dissolved in absolute alcohol gave a crystalline yellow potassium salt which on acidification yielded a yellow acid of m.p. 170-174° (dec.) (in some 16% yield calculated for $C_{14}H_{10}O_4$). If the yellow color of this acid proves to be real (i.e., not due to an impurity), the acid must be derived from a different component of Fraction A than is the amide; thus it might come from the next more abundant component of retention time 5.6 mins.

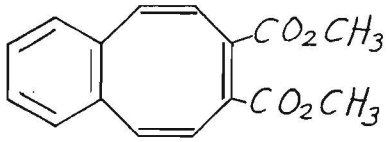
[1] Progress Report No. 1

The components of Fraction A have retention times in the range expected for one to one adducts of naphthalene and dimethyl acetylenedicarboxylate ($C_{16}H_{14}O_4$) since dibutyl phthalate ($C_{16}H_{22}O_4$) and dimethyl naphthalene-2,3-dicarboxylate ($C_{14}H_{12}O_4$) have rather similar retention times. The following structures are among those under consideration for these adducts.









The work described here is largely that of the chief investigator. On September 1, Mr. Thomas C. Campbell (a graduate student in the School of Chemistry) started work on this project and on October 1, Mr. Gerald Cohn (also a graduate student) will begin work. With the aid of these two assistants, it is hoped that we will be able to pursue our chief objectives with the energy and diligence which the problem deserves.

Respectfully submitted,

Erling Grovenstein, Jr.
Project Director

Approved:

for Frederick Bellinger, Chief
Chemical Sciences & Materials Division

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

June 22, 1964

Commanding Officer
U. S. Army Research Office (Durham)
Box CM, Duke Station
Durham, North Carolina

Subject: Progress Report No. 4, Project No. A-606
"Photochemically Induced Reactions of Acetylenes with Aromatic Compounds"
Covering the Period September 21, 1963 to June 20, 1964
Grant No. DA-ARO(D)-31-124-G258

Gentlemen:

Work has continued on the photochemical reaction between naphthalene and dimethyl acetylenedicarboxylate. Solvent precipitation of the crude product from solution in chloroform by addition of petroleum ether has been found to provide a simple separation of polymeric material from products of low molecular weight. The polymeric material evidently comes largely from a photo-induced polymerization of dimethyl acetylenedicarboxylate, since a material of similar physical properties is obtained by irradiation of the ester in methanol solution in absence of naphthalene. In contrast to the facile photochemical reactions which have been observed, there appears to be no appreciable amount of thermal reaction between molten naphthalene and dimethyl acetylenedicarboxylate at 100° on a steam bath for 24 hours in absence of solvent. Chromatography of the photo-product of naphthalene and dimethyl acetylenedicarboxylate on acid-washed alumina seems to hold promise as a means of separation of the complex mixture of products.

Only traces of cyclooctatetraene have been found in all attempted photochemical reactions between benzene and acetylene, with or without

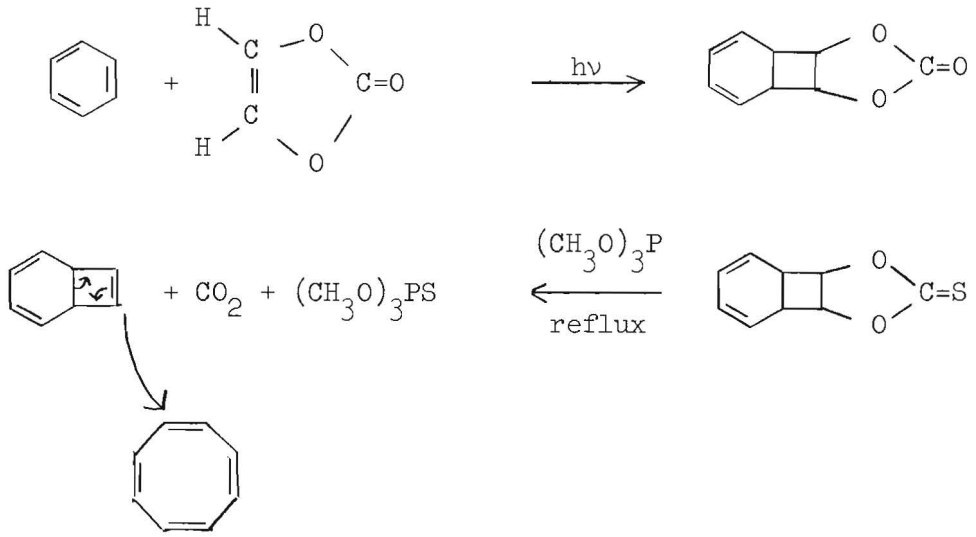
acetone as a solvent and with full illumination from a mercury-vapor lamp in a quartz apparatus. A test experiment demonstrated, however, that cyclooctatetraene was unstable under these conditions. While test experiments demonstrated that cyclooctatetraene was decomposed to less than 10 per cent in acetone as solvent (with or without the presence of small amounts of benzophenone) when the mercury-vapor light was filtered through a pyrex filter, again at best only traces of cyclooctatetraene were detected in attempted reactions between benzene and acetylene under these conditions.

No photochemical reaction between naphthalene and acetylene has been observed under a variety of conditions (in acetone or in methanol solution, with or without a pyrex filter, with or without addition of benzophenone). When methanol and benzophenone were both present, however, at least 12 per cent yield of 1,1-diphenylethan-1,2-diol was formed as proved by product isolation. This rather high yield of the methanol addition product of benzophenone is somewhat surprising since benzophenone and isopropyl alcohol on irradiation with sunlight give a 94 to 95 per cent yield of isolable benzopinacol (Org. Syn. Coll. Vol. II, p. 71). It would seem to be of interest to investigate in more detail by modern means the photochemical reactions between alcohols and ketones.

The essentially negative results attained so far on attempted photochemical reactions between acetylene and benzene or naphthalene prompted us to look for a photo-reaction between anthracene and acetylene. However, no evidence for such a reaction has been obtained in acetone as solvent with a pyrex filter (much of the photo-dimer of anthracene was obtained) or in

carbon disulfide as solvent in a pyrex reaction cell (much decomposition of carbon disulfide was observed).

Since acetylene is the simplest compound containing a triple bond whose photochemical reaction with aromatic compounds would be of special interest, some thought and work has been devoted to a possible alternative method of introducing an acetylene unit indirectly into aromatic compounds by photochemical methods. One possibility is the following scheme as illustrated for benzene:



This synthetic approach was suggested by Corey and Winter's recent report (J. Am. Chem. Soc., 85, 2677 (1963)) on the formation of olefins from cyclic thionocarbonates by reaction with trialkyl phosphites.

Since a sample of chlorovinylene carbonate was available, its photoreaction with benzene was first investigated. Irradiation in a quartz apparatus with unfiltered light from a mercury vapor lamp under a nitrogen atmosphere gave about 50 per cent yield of vinylene carbonate; about the

same yield of vinylene carbonate was observed under similar conditions in presence of benzophenone. When chlorovinylene carbonate was irradiated in cyclohexane solution with the same unfiltered light, about 90 per cent yield of vinylene carbonate was obtained. Few other examples appear to be known of the photochemical replacement of chlorine by hydrogen in organic compounds in good yield.

Phenanthrene when irradiated in methanol solution containing dimethyl acetylenedicarboxylate gave a good yield of adduct whose purification and identification is in progress.

Since frequently as part of the process of isolation and purification of photo-adducts of dimethyl acetylenedicarboxylate, it is necessary to remove the methyl groups by saponification, an attempt has been made to see if the monopotassium salt of acetylenedicarboxylate can be added to benzene. Irradiation of an aqueous methanolic solution containing both benzene and monopotassium acetylenedicarboxylate under a nitrogen apparatus in a quartz apparatus gave a product which, however, has proved hard to handle in view of its ready thermal decomposition.

Throughout the period of the present report, Mr. Thomas C. Campbell (a Ph.D. candidate in the School of Chemistry) has served as research assistant; and for part of this time, Mr. Gerald Cohn (October 1, 1963 - March 16, 1964) and Mr. William J. Burroughs (April 1 - May 31, 1964) have served in the same capacity.

We regret that through an oversight on our part, this report, which was due March 31, 1964, is so late in preparation.

Respectfully submitted,

for Erling Grovenstein, Jr.
Project Director

GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

October 1, 1964

Commanding Officer
U. S. Army Research Office (Durham)
Box CM, Duke Station
Durham, North Carolina

Subject: Progress Report No. 5, Project No. A-606
"Photochemically Induced Reactions of Acetylenes with Aromatic Compounds"
Covering the Period June 21, 1964 to September 30, 1964
Grant No. DA-ARO(D)-31-124-G258

Gentlemen:

Work has continued on the photochemical reaction between naphthalene and dimethyl acetylenedicarboxylate. Use of cyclohexane as a solvent in place of methanol gives a somewhat simpler, less highly colored product which contains a higher proportion of the one to one adduct. This adduct undergoes pyrolysis in our Perkin-Elmer VPC apparatus at about 250° with formation of much naphthalene, a little dimethyl acetylenedicarboxylate, and other unknown products. The one to one adduct can be separated from other products by chromatography on alumina; however, thin film chromatography indicates that a mixture of one to adducts is in fact formed. We hope that preparative thin film chromatography may be able to resolve this mixture into its individual components.

The interpretation of our previous negative experiments on reaction of acetylene with benzene was complicated since, in the case of full illumination with the mercury-vapor lamp in quartz apparatus, the expected product of the reaction, cyclooctatetraene, was found to be readily destroyed. To overcome this difficulty, at the suggestion of

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Dr. R. G. Ghirardelli, we have looked for a photochemical reaction between acetylene and dimethyl phthalate. Irradiation of these reactants in acetone solution in quartz apparatus for 20 hours gave no detectable (less than 0.6% yield) dimethyl 1,2-cycloöctatetraenedicarboxylate. Since this product has been made in our laboratory by similar photochemical reaction of dimethyl acetylenedicarboxylate with benzene, the present negative result gives added emphasis to the difficulty (or impossibility?) of obtaining photochemical additions of acetylene itself.

In previous work (Progress Report No. 4) on attempts to photosensitize reactions of acetylene by use of benzophenone, it was discovered that the methanol (used as solvent) underwent photochemical addition to benzophenone to give 1,1-diphenylethan-1,2-diol. This result was rather surprising since benzophenone and isopropyl alcohol on irradiation with sunlight give a 94 to 95 per cent yield of isolable benzopinacol (Org. Syn. Coll. Vol. II, p. 71). We have now looked at the photochemical addition of methanol, ethanol, and 2-propanol to benzophenone in more quantitative detail with analyses being made by vapor phase chromatography and ultraviolet spectroscopy (for unreacted ketone). Our preliminary, semiquantitative results are recorded in Table I. Two generalizations can be drawn from this table: first, the tendency for addition of alcohols to benzophenone to give unsymmetrical glycols as opposed to benzopinacol decreases along the series $CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH$; second, intense light of in part shorter wave length (full mercury arc, quartz vessel) gives more of the unsymmetrical glycol and less

TABLE I

Photochemical Reactions of Benzophenone with Alcohols

Product	Conditions: Sunlight 3 Weeks Pyrex Vessel	Hg Lamp 20 Hours Pyrex Filter	Hg Lamp 3 Hours Quartz Cell	Hg Lamp 20 Hours Quartz Cell
	With Methanol			
$Ph_2C(OH)CH_2OH$	36.2%	11.3%	33.0%	85.2%
$Ph_2C(OH)C(OH)Ph_2$	49.6%	53.5%	None	14.8%*
Ph_2CO	14.2%	35.2%	67.0%	
	With Ethanol			
$Ph_2C(OH)CH(OH)CH_3$	≈ 0.1%	≈ 0.2%	25.6%	32.2%
$Ph_2C(OH)C(OH)Ph_2$	89.9%	94.6%	19.0%	67.8%*
Ph_2CO	10.0%	5.2%	55.4%	
	With 2-Propanol			
$Ph_2C(OH)C(OH)(CH_3)_2$	None	None	5.8%	
$Ph_2C(OH)C(OH)Ph_2$	92.3%	97.9%	76.3%	
Ph_2CO	7.7%	2.1%	17.9%	

*Only the combined amount of benzopinacol and benzophenone was determined.

benzopinacol than does less intense light of longer wave length (sunlight or mercury arc with Pyrex filter). The first generalization can be rationalized by the mechanism of Pitts and co-workers (J. Am. Chem. Soc., 81, 1068 (1959)); however, the second generalization appears to demand a different mechanism for reaction promoted by light of shorter wave length or alternatively, the differences with light sources are due to variations of light intensity and of absorptivity of light of different wave lengths.

Throughout the period of the present report, Mr. Thomas C. Campbell and Mr. Frank W. Walker have served as research assistants.

Respectfully submitted,

Erling Grovenstein, Jr.
Project Director

FINAL REPORT

PROJECT A-606

PHOTOCHEMICALLY INDUCED REACTIONS OF ACETYLENES WITH AROMATIC COMPOUNDS

By Erling Grovenstein, Jr.

Department of the Army Project No. 009925001
U. S. Army Research Office (Durham) Project No. 3520-C
Grant No. DA-ARO(D)-31-124-G258

January 3, 1962 to July 31, 1965

Prepared for
Department of the Army
U. S. Army Research Office
Durham, North Carolina

1965

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

FINAL REPORT

PROJECT A-606

PHOTOCHEMICALLY INDUCED REACTIONS OF ACETYLENES WITH AROMATIC COMPOUNDS

By

Erling Grovenstein, Jr.

DEPARTMENT OF THE ARMY PROJECT NO. 009925001
U. S. ARMY RESEARCH OFFICE (DURHAM) PROJECT NO. 3520-C
GRANT NO. DA-ARO(D)-31-124-G258

January 3, 1962 to July 31, 1965

Performed for
DEPARTMENT OF THE ARMY
U. S. ARMY RESEARCH OFFICE
DURHAM, NORTH CAROLINA

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SUMMARY

Irradiation with ultraviolet light of a mixture of benzene and acetylene under a variety of experimental conditions gave, at best, only a trace of cyclööctatetraene. No photo-adduct could be found of acetylene with dimethyl phthalate, naphthalene, or anthracene.

Vinylene carbonate underwent no detectable photochemical reaction with benzene. Chlorovinylene carbonate, however, upon irradiation in benzene or cyclohexane solution undergoes reduction to give vinylene carbonate in good yield.

Benzene with a solution of the monopotassium salt of acetylenedicarboxylic acid gives, upon ultraviolet irradiation, a different product from that obtained with dimethyl acetylenedicarboxylate.

Naphthalene, upon irradiation with a solution of dimethyl acetylene-dicarboxylate, gives a complex mixture of products which appear to be the result of an initial 1,2-addition of the acetylenic ester to the various aromatic multiple bonds of naphthalene. From the reaction mixture a crystalline derivative has been isolated which seems to have been derived from addition of dimethyl acetylenedicarboxylate to the 1,2-position of naphthalene. Furthermore, vapor phase chromatography (v.p.c.) provisionally indicates the presence of dimethyl phthalate, dimethyl naphthalene-2,3-dicarboxylate, dimethyl cyclööctatetraene-1,2-dicarboxylate, as well as naphthalene and dimethyl acetylenedicarboxylate in the purified reaction product. Since it was demonstrated that all of the naphthalene should have been removed by the purification process, the v.p.c. results indicate that the naphthalene adducts are undergoing pyrolysis under the conditions of the v.p.c. analysis. Reaction schemes are proposed to account for the observed products.

Preliminary experiments show that phenanthrene reacts readily with dimethyl acetylenedicarboxylate upon irradiation with ultraviolet light.

In experiments in which benzophenone was added as a photo-sensitizer, benzophenone was found to undergo addition of alcohol, especially methanol, to give considerable amounts of mixed pinacol, e.g., 1,1-diphenylethan-1,2-diol from methanol, in addition to the expected benzopinacol.

I. INTRODUCTION

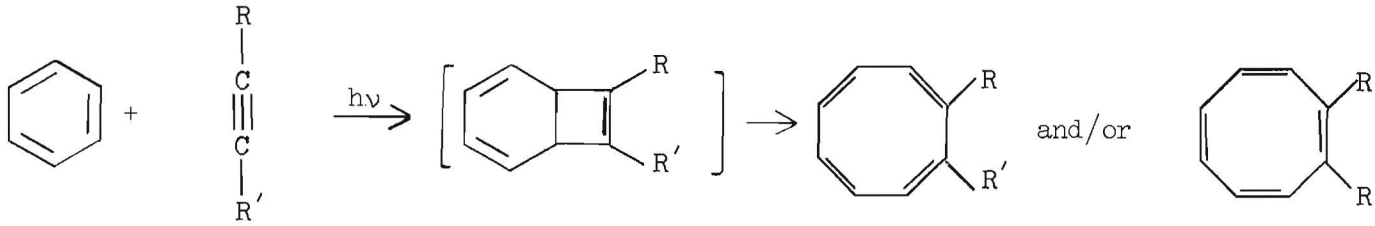
The general explanation of why many addition reactions which occur readily with unsaturated aliphatic compounds do not take place with aromatic compounds is that such reactions entail loss of a large amount of resonance energy on the part of the aromatic compound and, since sufficient energy is not liberated in the formation of new bonds, the reactions are, inconsequence, thermodynamically unfavorable. In some cases, reaction may be thermodynamically favorable at low temperatures but unfavorable at temperatures sufficiently high to promote reaction. It was our general intention in the present work to supply photochemically the energy needed for reaction. This research was undertaken primarily to broaden the general fund of knowledge concerning the nature and types of organic photochemical reactions which are feasible. In particular we looked for photochemical reactions of acetylene with benzene, naphthalene, anthracene, and dimethyl phthalate; of dimethyl acetylene-dicarboxylate with naphthalene and phenanthrene; of the monopotassium salt of acetylenedicarboxylic acid with benzene; of vinylene carbonate with benzene; of chlorovinylene carbonate with benzene and cyclohexane; and of benzophenone with methanol, ethanol, and 2-propanol.

Our original report[1] of the photochemical reaction of benzene with dimethyl acetylenedicarboxylate has been confirmed and elaborated upon by Bryce-Smith and Lodge[2] who have reported similar 1:1 photo-adducts of benzene with methyl propiolate and phenylacetylene. All of these reactions can be represented by the scheme:

---

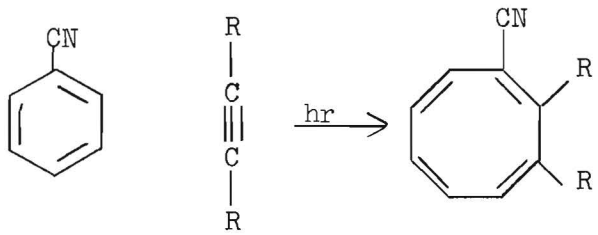
[1] E. Grovenstein, Jr., and D. V. Rao, Tetrahedron Letters, 148, 1961.

[2] D. Bryce-Smith and J. E. Lodge, Proc. Chem. Soc., 333 (1961); J. Chem. Soc., 695 (1963).



Under the same reaction conditions phenylacetylene also underwent photodimerization[2] to a 5:1 mixture of 1-phenylazulene and 1-phenylnaphthalene. These same workers also reported that when a slow current of dry acetylene was passed through an irradiated mixture of benzene (50 ml.) and acetone (110 ml.) at 52-56° for 29 hours, ca. 2 mg. of a product whose retention time was identical with that of cyclooctatetraene was produced. The significance of this latter observation is doubtful since acetylene has been observed to undergo photo-polymerization[3] in the gaseous state with ultraviolet light of wave lengths shorter than 2537 Å to give cyclooctatetraene as well as benzene and a small amount of styrene among the volatile products. It has been suggested[3] that cyclooctatetraene resulted from dimerization of intermediate cyclobutadiene in presence of a molecule of acetylene to take up the excess energy (three-body collision).

Büchi and co-workers[4] have reported that benzonitrile undergoes a photochemical reaction with 3-hexyne and 4-decyne in methanol solution to give 1:1 adducts according to the general process:



[2] Bryce-Smith and Lodge, op. cit.

[3] Z. Kuri and S. Shida, Bull. Chem. Soc. Japan, 25, 116 (1952); Z. Kuri, J. Chem. Soc. Japan, 76, 944 (1955).

[4] J. G. Atkinson, D.E. Ayer, G. Büchi, and E.W. Robb, J. Am. Chem. Soc., 85, 2257 (1963).

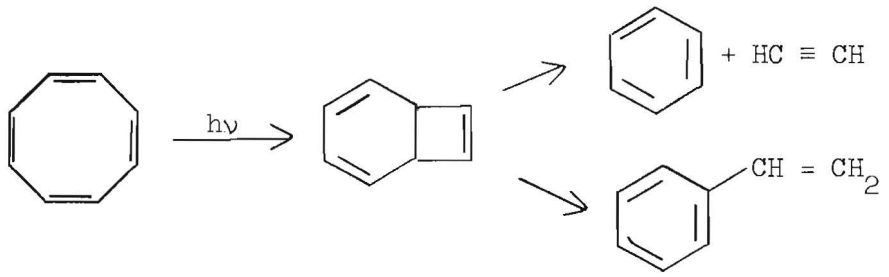
These workers surprisingly found that the yield of adduct was negligible upon irradiation of the pure liquid reactants in absence of the solvent methanol. Moreover benzonitrile failed to give any 1:1 photo-adducts in methanol solution with either acetylene or ethoxyacetylene. Furthermore, 3-hexyne failed[5] to give photo-adducts with either benzene or methyl benzoate under similar conditions.

[5]Atkinson, Ayer, Büchi, and Robb, op. cit.

II. RESULTS AND DISCUSSION OF PHOTOCHEMICAL REACTIONS

A. Benzene and Acetylene

Irradiation in a quartz cell of a solution of acetylene in a 50:50 mixture of benzene and acetone, under conditions such that the solution was kept saturated with a stream of acetylene, gave after 4 hours a solution containing about one volume of cyclooctatetraene in 10,000 volumes of solvent. The amount of cyclooctatetraene was not increased on increasing the irradiation time to 16 hours although the solution darkened in color. A test experiment indicated that cyclooctatetraene was, as nearly as could be judged, completely decomposed upon irradiation in the same solvent for 18 hours. Cyclooctatetraene has been reported[6] to decompose when irradiated in the vapor phase with 2537 Å light to give benzene and acetylene, an orange-colored liquid (possibly bicyclo[4,2,0]octatriene) which gives rise to polymer, and smaller amounts of styrene. The quantum yield of benzene and acetylene is about 0.10 and that of styrene 0.004[7]. Migirdicyan and Leach[8] have studied the photolysis of cyclooctatetraene at 77°K and have tentatively interpreted the reaction as follows:



[6] H. Yamazaki, Bull. Chem. Soc. Japan, 31, 677 (1958); H. Yamazaki and S. Shida, J. Chem. Phys., 24, 1278 (1958).

[7] I. Tanaka and M. Okuda, J. Chem. Phys., 22, 1780 (1954).

[8] E. Migirdicyan and S. Leach, Bull. Soc. Chem. Belges, 71, 852 (1962).

The photolysis of cyclo[8]octatetraene to benzene and acetylene as written above corresponds to the exact reversal of the reaction which we wished to study. Evidently in our experiments with acetylene and benzene we could get only a low stationary-state concentration of cyclo[8]octatetraene because of the facile reversal of the mode of formation. However, it remains for future experiments to prove that the trace of cyclo[8]octatetraene observed actually came by way of reaction of benzene with acetylene rather than by polymerization of acetylene or some other path.

Cyclo[8]octatetraene was found to be relatively stable toward ultraviolet light which had been filtered through Pyrex glass. Attempts to react benzene with acetylene by irradiation with such light in presence of benzophenone as an activator, however, gave no detectable cyclo[8]octatetraene.

B. Naphthalene and Acetylene

Irradiation of solutions of naphthalene in acetone saturated with acetylene in a quartz cell with light from a mercury vapor lamp failed to give any detectable reaction products of naphthalene with acetylene. Also, irradiation of naphthalene in alcoholic solutions saturated with acetylene with benzophenone as a photoactivator and with ultraviolet light filtered through Pyrex glass failed to yield any adduct of acetylene with naphthalene according to analysis by vapor phase chromatography; however, these experiments were complicated by photochemical reactions between benzophenone and alcohols used as solvent (see later discussion). No firm conclusion can be drawn from these negative experiments except that the correct experimental conditions have not been found to obtain the desired photochemical reaction. Hammond and Hardham[9] have noted that the quantum yield for addition of maleic

[9] G. S. Hammond and W. M. Hardham, Proc. Chem. Soc., 63 (1963).

anhydride to benzene with benzophenone as a sensitizer (380 mμ light) dropped off rapidly with reduction in concentration of benzene by addition of dioxane. Thus the most favorable condition for finding reaction between naphthalene and acetylene would seem to be the use of molten naphthalene with no solvent.

C. Anthracene and Acetylene

Irradiation (ultraviolet light filtered by Pyrex glass) of a solution of anthracene in acetone kept saturated with a stream of acetylene gave a crystalline solid identified as dianthracene but no adduct of acetylene with anthracene was detected.

Since singlet-triplet transitions can sometimes be induced by presence of atoms of high atomic number, anthracene was irradiated (Pyrex filter) in a carbon disulfide solution saturated with acetylene in hopes that the presence of carbon disulfide would facilitate getting anthracene in its triplet state[10], and that triplet anthracene might react with acetylene. Under the conditions tried, however, the solution became very dark and a black precipitate formed, evidently from photolysis of the carbon disulfide. The anthracene was recovered essentially unchanged after the photolysis.

D. Dimethyl Phthalate and Acetylene

In view of the fact that cyclooctatetraene has been found to be readily decomposed under all of the conditions so far investigated where traces of cyclooctatetraene could be detected in attempted photochemical reactions of acetylene with benzene, it was deemed desirable to attempt to react acetylene with a benzenoid compound whose product was reasonably stable under

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[10] Cf. E. J. Bowen, "Advances in Photochemistry," W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Editors, Interscience Publishers, New York, New York, 1963, pp. 36 and 38.

the conditions of irradiation. The most obvious choice is to attempt to react acetylene with dimethyl phthalate* since the hoped for product, dimethyl cyclöctatetraene-1,2-dicarboxylate, is known to be reasonably photo-stable, because it has been isolated in fair yield[11,12] from the photochemical reaction of dimethyl acetylenedicarboxylate with benzene. An attempted reaction of acetylene with dimethyl phthalate in acetone solution in a quartz cell with irradiation by a mercury vapor lamp, however, failed to yield any detectable dimethyl cyclöctatetraene-1,2-dicarboxylate, and dimethyl phthalate was recovered essentially unchanged. In retrospect, a more conclusive experiment would have been to irradiate acetylene in dimethyl phthalate in the absence of solvent; moreover, dimethyl cyclöctatetraene-1,2-dicarboxylate should be tested for stability under the particular set of experimental conditions (solvent, etc.) employed.

E. Vinylene Carbonate and Chlorovinylene Carbonate with Benzene and Cyclohexane

Since photo-addition of acetylene to aromatic compounds has been largely unsatisfactory or impossible under the conditions which have been investigated to date, and, yet, since addition of such a simple unit as acetylene to an aromatic compound would be of great potential interest, some thought and work has been devoted to a possible alternative method of introducing an acetylene unit indirectly into aromatic compounds by photochemical means. One possibility is the following scheme as illustrated for benzene:

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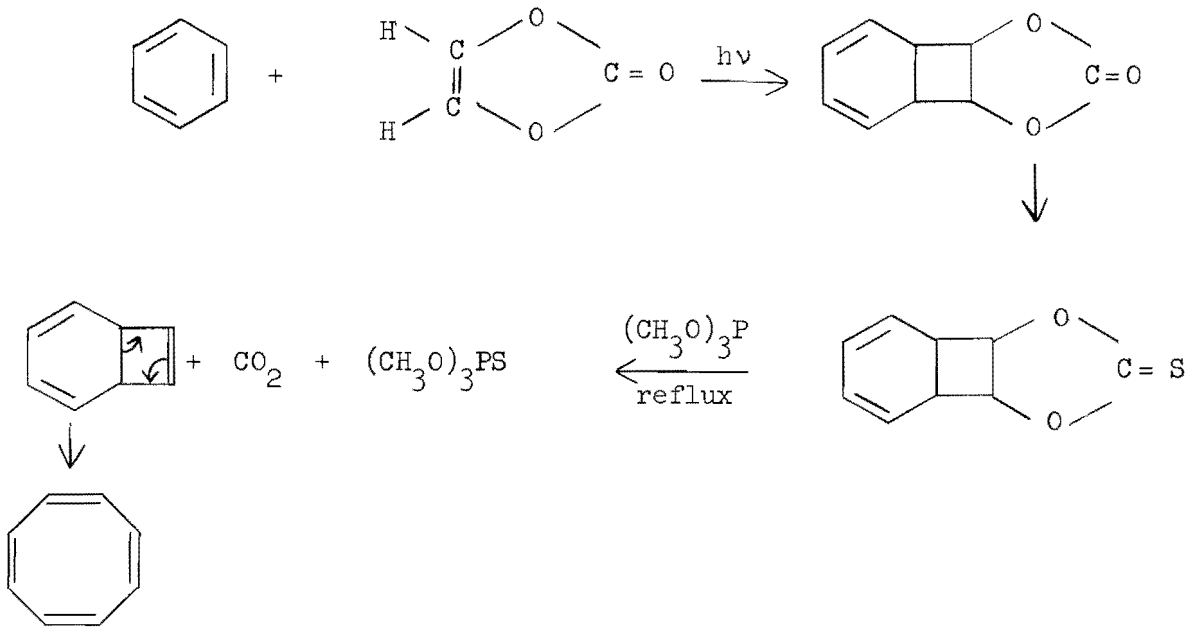
*We wish to thank Dr. R. G. Ghiradelli for suggesting this experiment.

[11]Grovenstein and Rao, op. cit.

[12]Bryce-Smith and Lodge, op. cit.



This synthetic approach was suggested by Corey and Winter's[13] recent, novel report on the formation of olefins from cyclic thionocarbonates by reaction with trialkyl phosphites. Irradiation of vinylene carbonate in benzene solution in a quartz cell under nitrogen for 18 hours, however, left the vinylene carbonate largely unaltered, and no evidence was obtained for any photo-adduct with benzene.

Since a sample of chlorovinylene carbonate was at hand, it too was irradiated in benzene solution in a quartz cell both with and without the presence of benzophenone. Under the conditions tried, some 50 and 60% of the chlorovinylene carbonate was converted into vinylene carbonate, and, again, no evidence was obtained for any photo-addition to benzene. When chlorovinelene carbonate was irradiated in cyclohexane solution, a still

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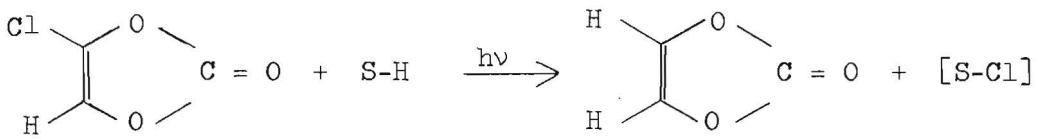
[13] E. J. Corey and R. A. E. Winter, J. Am. Chem. Soc., 85, 2677 (1963).

higher yield (some 90%) of vinylene carbonate was obtained. These photochemical reductions are provisionally represented by the following equation, where S-H is the solvent:



We are not aware of any comparable smooth replacement of chlorine by hydrogen in such high yield reported in the chemical literature.

F. Monopotassium Acetylenedicarboxylate and Benzene

Since the dimethyl ester of acetylenedicarboxylic acid has been found to react with benzene upon irradiation with ultraviolet light, it was deemed of interest to see if the monopotassium salt of acetylenedicarboxylic acid would undergo a similar reaction. To this end a homogeneous solution of the monopotassium salt was prepared in aqueous methanol containing some benzene and the solution irradiated for 20 hours under a nitrogen atmosphere. In one experiment the amorphous product which was isolated after acidification was found to show strong carbonyl absorption in addition to some absorption near that expected for a carboxylic acid. No evidence for formation of cyclöoctatetraene-1,2-dicarboxylic acid was obtained. In another experiment the reaction solution was found to undergo extensive decomposition during evaporation of solvents at steam bath temperature. The present work recalls the experiments of Bryce-Smith and Lodge[14] who, while able to react methyl propiolate with benzene under irradiation with ultraviolet light to give

[14] Bryce-Smith and Lodge, op. cit.

methyl cyclöoctatetraenecarboxylate, were unable to prepare cyclöoctatetraene-carboxylic acid by irradiation of propiolic acid in benzene.

G. Dimethyl Acetylenedicarboxylate and Naphthalene

Naphthalene has been found to undergo photochemical reaction with dimethyl acetylenedicarboxylate in acetone, methanol, and cyclohexane solutions. The products are reasonably similar in these three solvents but cyclohexane appears to give the simplest product mixture. The same reaction products are formed in methanol solution in a Pyrex cell as in a quartz cell though the yield is considerably reduced by use of a Pyrex cell. Since dimethyl acetylenedicarboxylate has its nearest absorption maximum at 270 mμ (ϵ = 189) while naphthalene has a strong broad maximum at 275 mμ ($\epsilon = 5 \times 10^3$) and weaker maxima at 311 mμ ($\epsilon = 8 \times 10^2$) and 320 mμ (ϵ = 22), photochemical activation of naphthalene or a naphthalene-dimethyl acetylenedicarboxylate complex evidently occurs.

The photochemical adduct after separation from reactants and high molecular weight material, finally by liquid phase chromatography from alumina, has been analyzed by vapor phase chromatography (v.p.c.). For the reaction run in cyclohexane, v.p.c. provisionally indicates the presence of dimethyl acetylenedicarboxylate, naphthalene, dimethyl phthalate, dimethyl cyclöoctatetraene-1,2-dicarboxylate, dimethyl naphthalene-2,3-dicarboxylate, and three components which are believed to be one-to-one adducts of dimethyl acetylenedicarboxylate and naphthalene. The simultaneous presence of both naphthalene and dimethyl acetylenedicarboxylate in a product which has been so carefully purified strongly implies that the adduct has undergone partial pyrolysis during the vapor chromatography. It was in fact demonstrated that naphthalene should have been completely removed from the photo-adduct by the liquid chromatographic procedure. The explanation

for the presence of dimethyl cyclo[8]octatetraene-1,2-dicarboxylate is in some doubt. This product is the normal product of reaction of the acetylenic ester with benzene; however, an ultraviolet spectroscopic examination of the purified cyclohexane used in the present work failed to reveal any benzene.

The reaction scheme of Chart I is suggested to account for the reaction products. The initial reaction is an addition of dimethyl acetylene-dicarboxylate to the 1,2-, 2,3-, 1,9-, or 9,10-position of naphthalene. By analogy with the addition[15] of dicyanomethylene to naphthalene, the major product of addition would be expected to be to the 1,2-position with lesser amounts of addition to the 2,3- and 1,9-positions of naphthalene. We have in fact succeeded in isolating an N,N′-dibenzylamide of our photo-adduct of naphthalene which has satisfactory elementary analysis for such a 1:1 adduct. Moreover, the ultraviolet absorption spectrum of our derivative [λ_{max} 227 mμ (ϵ 7.6 x 10^4) and 288.5 mμ (ϵ 1.0 x 10^4)] is similar to that [λ_{max} 227 mμ (ϵ 2.5 x 10^4) and 272 mμ (ϵ 7.9 x 10^3)] reported[16] for the adduct of dicyanomethylene to the 1,2-position of naphthalene. Finally, the nuclear magnetic resonance (n.m.r.) spectrum is also in accord with structure I for the adduct from which our crystalline derivative is derived (see Experimental Details).

Chart I also shows plausible paths to dimethyl naphthalene-2,3-dicarboxylate, dimethyl phthalate and other products which are conceivably present but not yet identified. The proposed path leading to dimethyl cyclo[8]octatetraene-1,2-dicarboxylate is unusual; better explanations may exist for the presence of this product (see previous discussion).

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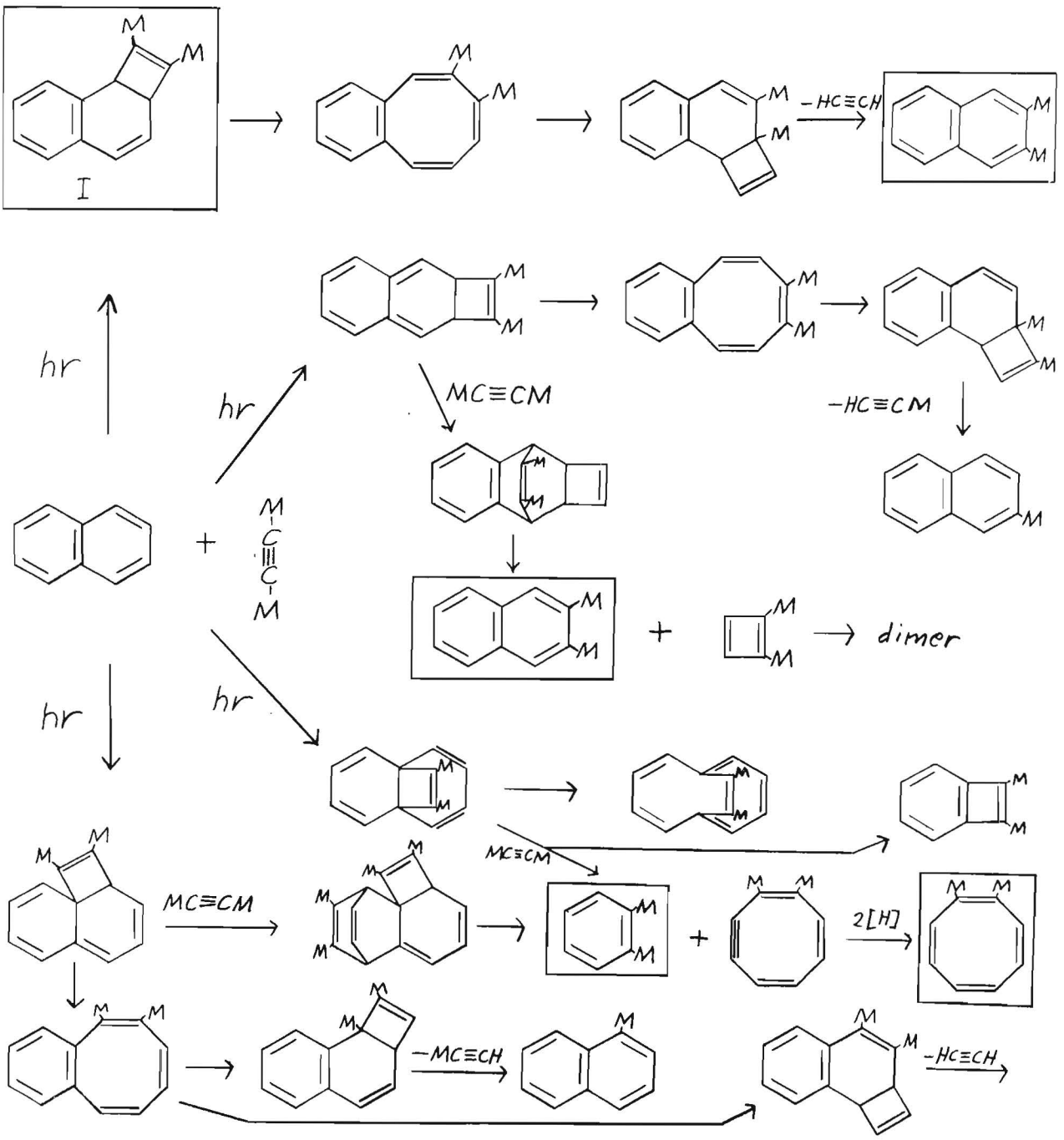
[15] E. Ciganek, J. Am. Chem. Soc., 87, 652 (1965).

[16] Ciganek, loc. cit.

Chart I

Possible Photochemical Reactions of Naphthalene
with Dimethyl Acetylenedicarboxylate

Note: The compounds which have so far been identified are enclosed in square blocks; M = $-CO_2CH_3$



H. Phenanthrene and Dimethyl Acetylenedicarboxylate

Preliminary experiments on irradiation of solutions of phenanthrene and dimethyl acetylenedicarboxylate in methanol show that a photo-chemical adduct is formed; however, the product has not been investigated extensively.

I. Benzophenone with Methanol, Ethanol, and 2-Propanol

Irradiation of solutions of benzophenone in methanol, ethanol, and 2-propanol with ultraviolet light from an unfiltered mercury-vapor lamp gives increasing amounts of benzopinacol, other conditions being the same, on going from the first to the last solvent cited. Conversely methanol gives the most and 2-propanol the least mixed pinacol from addition of the solvent to benzophenone:

$$Ph_2CO + RR'CHOH \longrightarrow Ph_2C(OH)C(OH)RR'$$

Benzopinacol, under similar conditions, undergoes little photolysis.

III. EXPERIMENTAL DETAILS

The apparatus for irradiation was made by Hanovia Chemical and Manufacturing Company of Newark, New Jersey, and contained a high pressure quartz mercury lamp (type LL) of 30 cm. arc length. The lamp operated on about 1000 watts at a current of 3.8 to 4.2 amperes and was surrounded by a cylindrical, water-cooled cell which contained a solution of the substances to be irradiated. This cell was made either of quartz or of Pyrex glass. The quartz cell was used except where otherwise specified in this report. In some experiments the quartz cell was employed with a cylindrical Pyrex glass filter separating the mercury lamp from the cell.

A. Irradiation of Acetylene in Benzene-Acetone Solution

A mixture of 150 ml. of benzene and 150 ml. of acetone was saturated with acetylene and then irradiated in the quartz cell under an atmosphere of acetylene which was maintained by slowly bubbling acetylene gas through the solution during irradiation. Small samples were withdrawn after 5, 6, 7, 8, 9, 13, and 15 hours of irradiation. Analysis of these by vapor phase chromatography (Perkin-Elmer Column R) indicated that the concentration of cyclooctatetraene in all of these solutions was about one part in ten thousand and did not change appreciably over the time interval of 5 to 15 hours. Repetition of this experiment on a 50:50 mixture of benzene-acetone previously saturated with acetylene at 7 lb./in.^{2} gauge pressure gave essentially the same concentration of cyclooctatetraene after both 4 and 16 hours of irradiation. A final repetition of irradiation of a saturated solution of acetylene in 50:50 benzene-acetone but without sweeping with acetylene or other extensive precautions to keep out air gave after 18 hours a red-brown solution with about the same trace amount of cyclooctatetraene.

B. Irradiation of Acetylene in Benzene Solution

Three hundred milliliters of benzene (anhydrous, thiophene-free) was saturated with acetylene and the solution was irradiated in a quartz cell for 20 hours. The solution acquired a yellow color and a brown polymeric film formed on the walls of the cell. A small amount of a white solid material [m.p. > 350° (dec.)] was obtained. A trace of cyclooctatetraene was present in the benzene solution according to v.p.c. analysis.

C. Irradiation of Cyclooctatetraene

A solution of 1.7 ml. of cyclooctatetraene in a solution of 150 ml. of acetone and 150 ml. of benzene was irradiated in the quartz cell for 18 hours. Examination of the final solution by v.p.c. indicated that at least 95% of the cyclooctatetraene (retention time 6.7 min.) had been destroyed. A new peak appeared in the vapor chromatogram at 11.7 min.

D. Irradiation of Cyclooctatetraene with Near U.V. Light

Cyclooctatetraene (3.0 g.) in 90 ml. of benzene and 180 ml. of acetone was irradiated for 20 hours in a quartz cell with ultraviolet light which had been passed through a Pyrex glass filter. Analysis of the resulting solution (v.p.c.) indicated that at least 90% of the cyclooctatetraene remained undecomposed. Repetition of this experiment, but with 1.0 g. of benzophenone present, gave after 19 hours of irradiation practically no decomposition of cyclooctatetraene according to v.p.c. analysis.

E. Irradiation of Acetylene with Near U.V. Light in a Benzene-Acetone Solution in Presence of Benzophenone

A solution of benzophenone (1.50 g.) in 100 ml. of benzene and 200 ml. of acetone was saturated with acetylene and then irradiated for 20 hours

in a quartz cell with ultraviolet light which was filtered through Pyrex glass (u.v. cut-off about 300 mμ). No cyclöoctatetraene was detectable by v.p.c. analysis on the concentrated solution. A repetition of this experiment but with a stream of acetylene bubbling through the solution during irradiation likewise gave no cyclöoctatetraene in the residual solution after removal of most of the solvent through a 12 in. packed column. The latter experiment was repeated with 3.0 g. of benzophenone in 300 ml. of pure benzene with an irradiation time of 72 hours but again no cyclöoctatetraene was detected in the concentrated residual solution.

F. Irradiation of Naphthalene and Acetylene

Naphthalene (5.0 g.) was dissolved in 350 ml. of acetone. The solution was saturated with acetylene and then irradiated for 22 hours with a slow stream of acetylene passing through the solution. The solvent was removed on a rotating evaporator and the residue analyzed by v.p.c. The small peaks which were observed with retention times greater than that of naphthalene were shown to be impurities in the starting naphthalene. A repetition of this experiment in methanol as solvent with irradiation for 42 hours likewise failed to give any photochemical products of longer retention time than naphthalene. The experiment in methanol was repeated but with light filtered through Pyrex glass; again no photo-products of retention times greater than naphthalene were detected.

Attempts were then made to see if reaction could be induced with benzophenone as a photochemical activator with ultraviolet light filtered through Pyrex glass. In a typical experiment 5.0 g. of naphthalene, 2.0 g. of benzophenone, and 350 ml. of methanol saturated with acetylene were irradiated for 22 hours with filtered light while a slow stream of

acetylene bubbled through the solution. The solvent was removed on a rotating evaporator. Analysis of the residue by v.p.c. showed that all of the peaks of retention time greater than naphthalene could be accounted for either by impurities in the naphthalene or by the benzophenone and products derived therefrom (benzopinacol and 1,1-diphenylethane-1,2-diol). Analogous experiments run in isopropyl alcohol, t-butyl alcohol, and t-amyl alcohol as solvent gave similar results.

G. Irradiation of Anthracene and Acetylene

Anthracene (5.0 g., m.p. 215-216°) was dissolved in 350 ml. of acetone which was saturated with acetylene. The solution was irradiated for 18 hours with light filtered through Pyrex glass while acetylene was slowly bubbled through the solution. The final reaction mixture contained a copious white precipitate which was removed by filtration and washed with acetone and hot benzene. The precipitate amounted to 2.1 g. of material of m.p. 237-241° (dec.) and is identified as dianthracene (reported m.p. 242-244°). Analysis by v.p.c. of the solution after removal of dianthracene revealed the presence of anthracene but no material of longer retention time, as expected for an adduct of acetylene, was detected.

In another experiment 3.0 g. of anthracene was dissolved in 650 ml. of freshly distilled carbon disulfide saturated with acetylene and the solution irradiated for 18 hours in a Pyrex cell while a stream of acetylene was bubbled through the solution. The irradiated solution was black and a black precipitate was suspended in it. The black precipitate was separated by filtration and washed with carbon disulfide; the black precipitate did not melt on the end of a spatula but did finally burn when heated. After removal of carbon disulfide from the remaining solution, a black residue

was deposited; this residue was soluble in benzene. A v.p.c. analysis of the residue showed that it was at least 98% anthracene, and no peaks of longer retention time were observed.

H. Irradiation of Dimethyl Phthalate and Acetylene

Dimethyl phthalate (5.13 g.) was dissolved in 300 ml. of acetone saturated with acetylene and the solution, in a quartz cell, was kept saturated with acetylene by bubbling in acetylene gas while the mixture was irradiated with ultraviolet light for 20 hours. The solvent was removed on a rotating evaporator to yield 5.17 g. of a slightly yellow liquid. Analysis of this liquid by v.p.c. showed the presence of less than 0.6% (if any) of dimethyl cycloöctatetraene-1,2-dicarboxylate and recovery of dimethyl phthalate essentially unchanged. A known sample of dimethyl cycloöctatetraene-1,2-dicarboxylate was available for comparison of retention times.

I. Irradiation of Vinylene Carbonate in Benzene and Cyclohexane

Vinylene carbonate (1.5 ml.) was dissolved in 350 ml. of benzene and irradiated in a quartz cell under nitrogen for 18 hours. The benzene was removed on a rotating evaporator. A v.p.c. analysis of the residue showed that about 50% of the chlorovinylene carbonate was converted into vinylene carbonate and no peaks of longer retention time than these, such as might be expected for an adduct of benzene, were observed. This reaction was repeated with 1.5 g. of benzophenone present and an irradiation time of 18 hours in the quartz cell. A v.p.c. analysis revealed that about 60% of the chlorovinylene carbonate had been converted to vinylene carbonate, and again no peaks of longer retention time than the reactants were observed.

In another experiment 3.0 ml. of chlorovinylene carbonate in 350 ml. of cyclohexane was irradiated under nitrogen in the quartz cell for 17 hours. The cyclohexane was removed on a rotating evaporator and v.p.c. analysis of the residue revealed that about 90% of the chlorovinylene carbonate had been converted into vinylene carbonate.

J. Irradiation of the Monopotassium Salt of Acetylenedicarboxylic Acid in Presence of Benzene

Monopotassium acetylenedicarboxylate (5.0 g.), methanol (275 ml.), water (100 ml.), and benzene (10 ml.) were mixed and found to give a homogeneous solution. Irradiation of this solution in the quartz cell under nitrogen for 20 hours was followed by concentration on a rotating evaporator to remove methanol and benzene. The cloudy solution which remained was diluted until clear with hot water and concentrated hydrochloric acid was added until no more precipitate formed. The precipitate was separated by filtration and the yellowish-brown amorphous precipitate was washed with cold water. An infrared spectrum of the dried precipitate in a potassium bromide disk showed carbonyl absorption and also probably carboxyl absorption. In a repetition of this experiment it was discovered that the product was decomposed even on evaporation of solvents at steam bath temperature.

K. Irradiation of Dimethyl Acetylenedicarboxylate and Naphthalene in Methanol

Naphthalene (20.0 g.) and dimethyl acetylenedicarboxylate (5.0 ml.) were dissolved in 300 ml. of methanol and the solution irradiated in the quartz cell for 48 hours. The solvent was removed *in vacuo* on a rotating evaporator at steam bath temperature with the vacuum being supplied by a

water pump. Finally, the vacuum was increased until the pressure read about 50 microns and at the same temperature the unreacted naphthalene was removed. The crude reaction product was dissolved in 7 ml. of chloroform and chromatographed from silica gel (Mallinkrodt) with chloroform-ethanol mixtures. The second and third fractions (with chloroform containing 0.1% ethanol) amounted to 0.96 g. of yellow-orange viscous oil; these two fractions are believed to contain the majority of 1:1 adduct. The total weight of all product removed from the column (finally with chloroform containing 8.1% ethanol) was 6.1 g. A portion (0.30 g.) of fraction 2 was heated at reflux for 2 hours with 3.0 ml. of benzylamine containing 0.10 g. of NH_4Cl. Some 15 ml. of water was added and the pH of the solution adjusted to 6 with 1M hydrochloric acid. The aqueous phase was separated from the tarry organic phase by decontation. The tar was washed once with water and then with n-hexane. The tar was taken up in hot ethyl alcohol and the solution treated with Nuclear C. There was obtained 0.080 g. of white cyrstals of m.p. 255-260° (dec.). Another sample of the same N-benzylamide (prepared from a sample of adduct which had been purified by distillation *in vacuo* and preparative vapor phase chromatography) was purified by three recrystallizations from acetonitrile and finally had m.p. 259.3-260.0°. This sample had the following analysis.

Anal. Calcd. for $C_{28}H_{24}N_2O_2$: C, 79.98; H, 5.75; N, 6.66;
Found: C, 79.62, 79.79; H, 5.39, 5.48; N, 6.73, 6.57.

The infrared spectrum of the two samples of N-benzylamide were identical and had maxima at 3.07 (N-H), 3.30 (aromatic and/or vinyl C-H), 3.43 (aliphatic C-H), 6.1 (carbonyl, amide I band) and 6.5 microns (amide II band). The ultraviolet absorption spectrum in ethanol had $\lambda_{max.}$ in mμ

and (ϵ) at 227 (7.6×10^4) and 288.5 (1.0×10^4) with fine structure (shoulders or maxima) at 269 (5.4×10^3), 278.5 (8.3×10^3), 292.5 (8.0×10^3), 300 (6.2×10^3), 306 (3.1×10^3), 316.5 (9.8×10^2), and 320 (8.3×10^2). The nuclear magnetic resonance spectrum in trifluoroacetic acid had proton chemical shifts in units of τ at the relative intensities given in parenthesis (expressed as number of hydrogen atoms): complex multiplets at 1.92-2.63 (17.5), singlet at 4.93 (2.2), and doublet (J = 5 cps) at 5.38 (4.3). In deuteriotrifluoroacetic acid the proton chemical shifts are similarly: complex multiplets with maxima 2.08 (0.8), 2.20 (1.1), 2.25 (0.8), 2.37 (1.1), 2.50 (2.0), and 2.63 (10.3), singlet at 4.95 (2.5), and singlet at 5.38 (4.1). The following structural assignments are made: two amide hydrogens at 1.92 τ, ten phenyl hydrogens at 2.63 τ, six possibly aromatic hydrogens at 2.2-2.5 τ, two hydrogens deshielded by vinyl and phenyl groups at 4.9 τ, and four benzylic hydrogens at 5.38 τ (which are spin split by the adjacent amide hydrogens in trifluoroacetic acid). This N-benzyl amide in acetone or acetonitrile solution did not decolorize a few drops of aqueous potassium permanganate. Also, the N-benzyl amide in acetonitrile solution did not decolorize a few drops of bromine in carbon tetrachloride.

A portion (0.46 g.) of fraction 2 of the photochemical adduct (see above) was added to 2.0 g. of potassium hydroxide in 30 ml. of ethanol. The resulting dark red solution was heated at the b.p. for one half hour. A yellow precipitate was removed by filtration. The precipitate dissolved readily in 5 ml. of water and acidification with 6 N hydrochloric acid gave 0.066 g. of orange-yellow powder. Recrystallization from aqueous ethanol gave 0.031 g. of orange-yellow compound of m.p. 209-217° (dec.).

L. Irradiation of Dimethyl Acetylenedicarboxylate and Naphthalene in Methanol with Use of Pyrex Filter

Naphthalene (40.7 g.) and dimethyl acetylenedicarboxylate (10 ml.) were dissolved in 600 ml. of methanol and irradiated in a Pyrex cell for 23 hours. The solvents and unreacted naphthalene and acetylenic ester were removed *in vacuo* (down to 50 μ) at steam bath temperature to give 0.96 g. of amber tar. For comparison of yields, 20.3 g. of naphthalene and 5.0 ml. of dimethyl acetylenedicarboxylate in 300 ml. of methanol were irradiated in a quartz cell for 20 hours; removal of solvents and reactants as previously left 3.8 g. of amber gum. Analyses of these amber gums by vapor phase chromatography indicated that the reaction run in a quartz cell gave about twelve times as much product of retention time in the range expected for one-to-one or one-to-two adduct as did the reaction run in a Pyrex cell; otherwise the composition of the reaction products was about the same.

M. Irradiation of Dimethyl Acetylenedicarboxylate and Naphthalene in Cyclohexane

Naphthalene (20.3 g.) and dimethyl acetylenedicarboxylate (5.0 ml.) were dissolved in 300 ml. of cyclohexane (purified by refluxing overnight with concentrated sulfuric acid and then distilling) and the solution irradiated in the quartz cell for 21 hours. After removal of reactants and solvents *in vacuo* at 100° in the usual manner, the product was largely dissolved in a little toluene and separated from 0.098 g. of solid by filtration; after removal of toluene, 1.89 g. of light amber oil remained. The amber oil was dissolved in 20 ml. of chloroform and then 500 ml. of petroleum ether was added. A precipitate formed (0.32 g. of m.p. 125-190° dec.)

and was removed by filtration. After evaporation of solvent 1.39 g. of light amber oil remained. The oil was dissolved, chromatographed on acid-washed alumina and eluted with benzene-acetone mixtures with fractions of 100 ml. being collected. The ninth fraction (0.188 g.), collected with an eluent of 95% benzene-5% acetone, contained the majority of the volatile product according to analysis by vapor phase chromatography, which gave products at the following retention times, relative to naphthalene, and relative peak areas recorded in parentheses: 0.46 (indeterminate peak area), 1.00 (5), 2.12 (1.5), 2.96 (32), 12.1 (32), 14.4 (4), 15.6 (11), 17.3 (16). The peak at 0.46 is dimethyl acetylenedicarboxylate; that at 1.00 is naphthalene, that at 2.12 is dimethyl phthalate; that at 2.96 is dimethyl cyclo$\ddot{o}$ctatetraene-1,2-dicarboxylate, that at 12.1 is dimethyl naphthalene-2,3-dicarboxylate, and those at 14.4, 15.6, and 17.3 are evidently one-to-one adducts of naphthalene with dimethyl acetylenedicarboxylate. These tentative structural assignments are based on comparisons of retention times with those of authentic samples. The v.p.c. of reaction products from a similar photochemical reaction with similar product purification but for a reaction run in methanol gave a similar product mixture save for absence of dimethyl cyclo$\ddot{o}$ctatetraene-1,2-dicarboxylate. However, the crude reaction mixture from use of cyclohexane as solvent gave a v.p.c. curve essentially identical with the product from fraction 9 above, while the crude product from use of methanol as solvent contained, in addition, strong unidentified v.p.c. peaks at retention times relative to naphthalene of 1.50 and 5.17.

Chromatography of 0.60 g. of naphthalene from acid-washed alumina according to the same procedure as used for naphthalene-dimethyl acetylenedicarboxylate product above gave most (0.57 g.) of the naphthalene

in the first fraction and the remainder in the second. Thus the naphthalene present in fraction 9 above must come from pyrolysis of the adduct in the vapor fractometer.

N. N, N'-Dibenzylnaphthalene-2,3-dicarboxyamide

The dimethyl ester (m.p. 47-39°) of naphthalene-2,3-dicarboxylic acid was allowed to react with benzylamine according to the procedure described previously for the naphthalene adduct of dimethyl acetylenedicarboxylate. There was obtained 1.3 g. of white crystals from 1.0 g. of the starting ester. After one recrystallization from acetonitrile the product had m.p. 203.0°. In 95% ethanol the amide had absorption maxima at 233 mμ (ϵ 7.8 x 10^4), 316 mμ (ϵ 7.3 x 10^2), and 329 mμ (ϵ 8.2 x 10^2) and shoulders at 268 mμ (ϵ 8.8 x 10^3) and 278 mμ (ϵ 7.0 x 10^3). The n.m.r. spectrum in trifluoroacetic acid had proton chemical shifts in units of τ at the relative intensities given in parentheses (expressed as number of hydrogen atoms): 1.25 (2.0), 1.73 (2.1), 2.12 (3.8), 2.52 (10.4), and 5.22 (3.8). These peaks are assigned respectively to the two amide hydrogens (this assignment was confirmed by disappearance of the 1.25 peak in CF_3CO_2D); H-1 and H-4 on naphthalene nucleus; H-5, H-6, H-7, and H-8 of the unsubstituted ring of naphthalene; ten aromatic hydrogens of the two N-benzyl groups; and four methylene hydrogens of the N-benzyl groups.

The n.m.r. spectrum of this N-benzylamide was observed to change significantly when the sample was allowed to stand overnight in trifluoroacetic acid. When 0.30 g. of the N-benzylamide was kept for 8 months in trifluoroacetic acid, the trifluoroacetic acid then removed at room temperature under partial vacuum, and the product recrystallized from aqueous ethanol, 0.11 g. of white crystals was obtained. After a further

recrystallization from ethanol, the compound had m.p. 211-212° and a mixed m.p. with the starting N,N'-dibenzyamide melted from 199 to 214°. The infrared spectrum of the product showed no N-H stretching and had two carbonyl absorption bands at 5.67 and 5.90 μ as expected for an imide. It is concluded, therefore, that the product is N-benzylnaphthalene-2,3-dicarboxylimide.

In contrast to this behavior the N-benzylamide derivative of the naphthalene adduct of dimethyl acetylenedicarboxylate showed no change in its n.m.r. spectrum on standing for 8 months in trifluoroacetic acid, and, moreover, the starting amide was recovered unchanged from the trifluoroacetic acid solution.

O. Irradiation of Phenanthrene and Dimethyl Acetylenedicarboxylate

Phenanthrene (7.1 g.) and dimethyl acetylenedicarboxylate (3.0 g.) were dissolved in 350 ml. of methanol and the solution was irradiated in the quartz cell for 18 hours. After the usual removal of solvent on the rotating evaporator, the residue (now essentially free of dimethyl acetylenedicarboxylate according to analysis by v.p.c.) was saponified by alcoholic potassium hydroxide. After the usual work-up procedure, 5.4 g. (76% of the starting material) of phenanthrene was recovered and 4.3 g. of crude acid was obtained. The acid, after further purification by precipitation from ethanol as its potassium salt, has been obtained as an ochre colored material of m.p. 215-235° (dec.).

P. Irradiation of Solutions of Benzophenone in Methanol, Ethanol, and 2-Propanol

Benzophenone (1 to 10 g.) in 325 ml. of methanol, ethanol, or 2-propanol was irradiated in the quartz cell, with and without a Pyrex filter or copper screen, for times of 5 minutes to 20 hours under an atmosphere of nitrogen.

The products have been analyzed by ultraviolet absorption to determine the concentration of benzophenone and by v.p.c. of the products after rearrangement to pinacolones to give the amount and types of photo-adducts. Because an unknown by-product is formed which absorbs in the ultraviolet in the region of benzophenone, the analysis for benzophenone is only approximate. Unfortunately, the amount of benzophenone must be known in order to interpret the v.p.c. results accurately, since the rearrangement products of some of the present pinacols are in part the same as that of benzophenone. We, therefore, have given only qualitative results in the present report.

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13. ABSTRACT

Irradiation with ultraviolet light of a mixture of benzene and acetylene under a variety of experimental conditions gave, at best, only a trace of cyclöoctatetraene. No photo-adduct could be found of acetylene with dimethyl phthalate, naphthalene, or anthracene.

Vinylene carbonate underwent no detectable photochemical reaction with benzene. Chlorovinylene carbonate, however, upon irradiation in benzene or cyclohexane solution undergoes reduction to give vinylene carbonate in good yield.

Benzene with a solution of the monopotassium salt of acetylenedicarboxylic acid gives, upon ultraviolet irradiation, a different product from that obtained with dimethyl acetylenedicarboxylate.

Naphthalene, upon irradiation with a solution of dimethyl acetylenedicarboxylate, gives a complex mixture of products which appear to be the result of an initial 1,2-addition of the acetylenic ester to the various aromatic multiple bonds of naphthalene. From the reaction mixture a crystalline derivative has been isolated which seems to have been derived from addition of dimethyl acetylenedicarboxylate to the 1,2-position of naphthalene. Furthermore, vapor phase chromatography (v.p.c.) provisionally indicates the presence of dimethyl phthalate, dimethyl naphthalene-2,3-dicarboxylate, dimethyl cyclöoctatetraene-1,2-dicarboxylate, as well as naphthalene and dimethyl acetylenedicarboxylate in the purified reaction product. Since it was demonstrated that all of the naphthalene should have been removed by the purification process, the v.p.c. results indicate

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that the naphthalene adducts are undergoing pyrolysis under the conditions of the v.p.c. analysis. Reaction schemes are proposed to account for the observed products.

Preliminary experiments show that phenanthrene reacts readily with dimethyl acetylenedicarboxylate upon irradiation with ultraviolet light.

In experiments in which benzophenone was added as a photo-sensitizer, benzophenone was found to undergo addition of alcohol, especially methanol, to give considerable amounts of mixed pinacol, e.g., 1,1-diphenylethan-1,2-diol from methanol, in addition to the expected benzopinacol.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Photochemistry						
Acetylene						
Dimethyl acetylenedicarboxylate						
Benzene						
Naphthalene						
Anthracene						
Phenanthrene						
Chlorovinylene carbonate						
Vinylene carbonate						
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